

Correlated metals and the LDA+U method

I. I. Mazin and A. G. Petukhov*

*Center for Computational Materials Science,
Naval Research Laboratory, Washington, DC 20375*

L. Chioncel and A. I. Lichtenstein

University of Nijmegen, NL-6525 ED Nijmegen, The Netherlands

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Abstract

While LDA+U method is well established for strongly correlated materials with well localized orbitals, its application to weakly correlated metals is questionable. By extending the LDA Stoner approach onto LDA+U, we show that LDA+U enhances the Stoner factor, while reducing the density of states. Arguably the most important correlation effects in metals, fluctuation-induced mass renormalization and suppression of the Stoner factor, are missing from LDA+U. On the other hand, for *moderately* correlated metals LDA+U may be useful. With this in mind, we derive a new version of LDA+U that is consistent with the Hohenberg-Kohn theorem and can be formulated as a constrained density functional theory. We illustrate all of the above on concrete examples, including the controversial case of magnetism in FeAl.

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*Permanent address: Dept. of Physics, South Dakota School of Mines and Technology, Rapid City, SD 57701

One of the most influential, from practical point of view, developments in the Density Functional Theory (DFT) in the last two decades was the LDA+U method (see, *e.g.*, Ref. [1]). This method includes the orbital dependence of the self-energy operators, missing from the Kohn-Sham potential, in a relatively crude, pseudo-atomic way, neglecting the fine details of the spatial variations of the Coulomb potential. On the contrary, the standard Local Density Approximation, LDA accounts for the spatial variation of the Hartree potential exceedingly well, but neglects the orbital dependence of the Coulomb interaction.

There is one inherent ambiguity in the LDA+U method: In LDA, all electron-electron interactions have already been taken into account in a mean field way. The Hubbard Hamiltonian that represents the underlying physics of the LDA+U method also incorporates a large part of the total Coulomb energy of the system. Simple combination of the LDA and Hubbard Hamiltonian thus leads to a double counting (DC) of the Coulomb energy, so one may want to identify those parts of the DFT expression for the total energy that correspond to the interaction included in the Hubbard Hamiltonian and subtract them. However, since the DFT Hamiltonian is written in terms of the total density, and the Hubbard Hamiltonian in the orbital representation, one cannot build a direct link between the two. Second, even if it were possible, that would be undesirable. Spatial variation of the Hartree and the exchange-correlation potentials is very important. It would be unreasonable to subtract that out just because it has been already taken into account elsewhere in a primitive way (roughly speaking, $UN^2/2$). Rather, one wants to identify the mean-field part of the Hubbard Hamiltonian, and subtract *that*, leaving only a *correction* to the LDA-type mean field solution.

This is not a uniquely defined procedure. Several recipes exist, and it has been appreciated lately [2] that the results of LDA+U calculations may depend crucially on the choice of the DC recipe. It should be noticed that while for strongly correlated systems the LDA+U ideology is at least practically established, in a relatively new area of applying LDA+U to moderately-correlated, metallic systems [2, 3, 4], the situation is very far from clear.

In this Letter we analyze the effect of different DC prescription on the LDA+U results in correlated metals. We also present a systematic approach to the DC problem, of which the existing recipes are special cases. Finally, we discuss which problems associated with this class of materials can, in principle, be solved within LDA+U, and which cannot.

We use for our analysis the spherically averaged form of the rotationally-invariant LDA+U

[5], due to Dudarev *et al.* [6]:

$$\begin{aligned}\Delta H_{LDA+U}^0 &= \frac{U}{2} \sum_{m\sigma \neq m'\sigma'} n_{m\sigma} n_{m'\sigma'} - \frac{J}{2} \sum_{m \neq m', \sigma} n_{m\sigma} n_{m'\sigma} \\ &= \frac{1}{2} U N^2 - \frac{1}{2} J \sum_{\sigma} N_{\sigma}^2 - \frac{1}{2} (U - J) \sum_{\sigma} \text{Tr}(\rho^{\sigma} \cdot \rho^{\sigma})\end{aligned}\quad (1)$$

where U and J are spherically averaged Hubbard repulsion and intraatomic exchange for electrons with the given angular momentum l , $n_{m\sigma}$ is the occupation number of the m -th orbital, $\sigma = \pm 1$ is the spin index, and the superscript 0 means that the double counting terms have not been subtracted yet. Here $\rho_{mm'}^{\sigma}$ is the orbital occupation matrix, $N_{\sigma} = \text{Tr}(\rho^{\sigma})$ and $N = \sum_{\sigma} N_{\sigma}$.

To subtract from Eq. (1) the DC term, one naturally starts with the first two terms in Eq. (1), *i.e.*, the Hartree and the Stoner energies. Both are explicit functionals of the spin density, and are likely to be better described by LDA. To identify the DC part of the last term of the Eq. (1), which explicitly depends on $n_{m\sigma}$, is less trivial; one needs to work out a “mean field” approximation to this term, that is, substitute $\text{Tr}(\rho^{\sigma} \cdot \rho^{\sigma})$ by some quantity x_{σ} that depends solely on total spin density. Czyżyk and Sawatzky [7] suggested that x_{σ} should be equal to $\text{Tr}(\rho^{\sigma} \cdot \rho^{\sigma})$ in the limit of the uniform occupancy, $\rho_{mm'}^{\sigma, LDA} = \delta_{mm'} n_{\sigma}$, and, consequently, $x_{\sigma} = (2l + 1)n_{\sigma}^2$, where $n_{\sigma} = N_{\sigma}/(2l + 1)$. This leads to the following corrections to the total energy and the effective potential:

$$\begin{aligned}\Delta E_{LDA+U}^{AMF} &= -\frac{U - J}{2} \sum_{\sigma} \text{Tr}(\delta \rho^{\sigma} \cdot \delta \rho^{\sigma}) \\ \Delta V_{LDA+U}^{AMF}(mm'\sigma) &= -(U - J) (\rho_{mm'}^{\sigma} - n_{\sigma} \delta_{mm'}).\end{aligned}\quad (2)$$

Here AMF stands for “Around Mean Field” [7] and $\delta \rho_{mm'}^{\sigma} = \rho_{mm'}^{\sigma} - n_{\sigma} \delta_{mm'}$.

For strongly correlated systems the limit of the uniform occupancy is not correct (in fact, it is not correct even in weakly correlated systems, due to the crystal field). Thus, it is not surprising that for the systems with strongly localized electrons the AMF functional leads to rather unrealistic results. This observation led [7, 8] to another prescription, $x_{\sigma} = (2l + 1)n_{\sigma}$,

$$\begin{aligned}\Delta E_{LDA+U}^{FLL} &= -\frac{U - J}{2} \sum_{\sigma} (\text{Tr}(\rho^{\sigma} \cdot \rho^{\sigma}) - (2l + 1)n_{\sigma}) \\ \Delta V_{LDA+U}^{FLL}(mm'\sigma) &= -(U - J) \left(\rho_{mm'}^{\sigma} - \frac{1}{2} \delta_{mm'} \right),\end{aligned}\quad (3)$$

which produces the correct behavior in the fully localized limit (FLL) where $n_{m\sigma} = 0$ or 1.

Most of the modern LDA+U calculations utilize one of these two functionals, although in real materials the occupation numbers lie between these two limits.

In the AMF the LDA+U correction to the electronic potential, Eq. 2, averaged over all occupied states, is zero. This is a possible way to define a mean field (cf. the Slater approximation to the Fock potential), but not the way used in the DFT. The latter is a mean field theory that produces the correct total energy, not the correct average potential. AMF and FLL represent the “DFT” mean field if all occupation numbers are all the same, or are all 0 or 1, respectively. It is easy to show that $(2l+1)n_\sigma^2 \leq \text{Tr}(\rho^\sigma \cdot \rho^\sigma) \leq (2l+1)n_\sigma$, so that AMF always gives a negative, and FLL a positive correction to the total energy, while the right (in the DFT sense) recipe should give zero correction to the total energy. That can be achieved by using a linear interpolation between the two extremes corresponding to AMF and FLL, $x_\sigma = (2l+1)(\alpha n_\sigma + (1-\alpha)n_\sigma^2)$, where $0 \leq \alpha \leq 1$, and

$$\Delta E_{LDA+U}^{DFT} = -\frac{U-J}{2} \sum_{\sigma} [\text{Tr}(\delta\rho^\sigma \cdot \delta\rho^\sigma) - (2l+1)\alpha n_\sigma(1-n_\sigma)]$$

$$\Delta V_{LDA+U}^{DFT}(mm'\sigma) = -(U-J) \left[\rho_{mm'}^\sigma - \left((1-\alpha)n_\sigma + \frac{\alpha}{2} \right) \delta_{mm'} \right]. \quad (4)$$

In the spirit of the DFT, $\Delta E_{LDA+U}^{DFT} = 0$, so

$$\alpha = \frac{\sum_{\sigma} \text{Tr}(\delta\rho^\sigma \cdot \delta\rho^\sigma)}{(2l+1) \sum_{\sigma} n_\sigma(1-n_\sigma)} \quad (5)$$

We emphasize that α is not adjustable, nor is it a formal functional of the charge density, but it is a material-dependent parameter (like, say, U itself), defined by the *self-consistent* occupation matrix. However, in practical calculations it is better to recompute α after each iteration, as the current value of $\rho_{mm'}^\sigma$ changes. Note that the total energy is given by the regular LDA expression that only implicitly depends on U and J *via* the changing density distribution; it is variational with respect to the charge density at a fixed α , but *not* variational with respect to α itself. The fact that this prescription is derived according to the DFT ideology allows one to formulate the proposed LDA+U functional (unlike the existing LDA+U functionals) as a *constrained DFT theory* [9] at a given α , with the constraint given by Eq. (5). $(U-J)/2$ appears then as a Lagrange multiplier.

We have tested the proposed functional (4) on NiO, a prototypical compound for LDA+U calculations (see, e.g., [10]). Fig. 1 shows the band gap and the magnetic moment of NiO as a function of U at $J = 0.95$ eV for three different functionals (Eqs. 2, 3, and 4), calculated

within the linear-muffin-tin orbital (LMTO) method in the atomic sphere approximation (ASA). The parameter $\alpha \simeq 0.5$ is almost independent on U . Accordingly, the results of our calculations based on Eq. 4 for both band gaps and magnetic moments lie right between those for AMF and FLL calculations, and the effect of U is reduced compared to the FLL calculations. This is in accord with a known observation [10] that in NiO the FLL LDA+U gives the best agreement with the experiment for $U \lesssim 6$ eV, smaller than $U \simeq 8$ eV calculated from the first principles[10, 11].

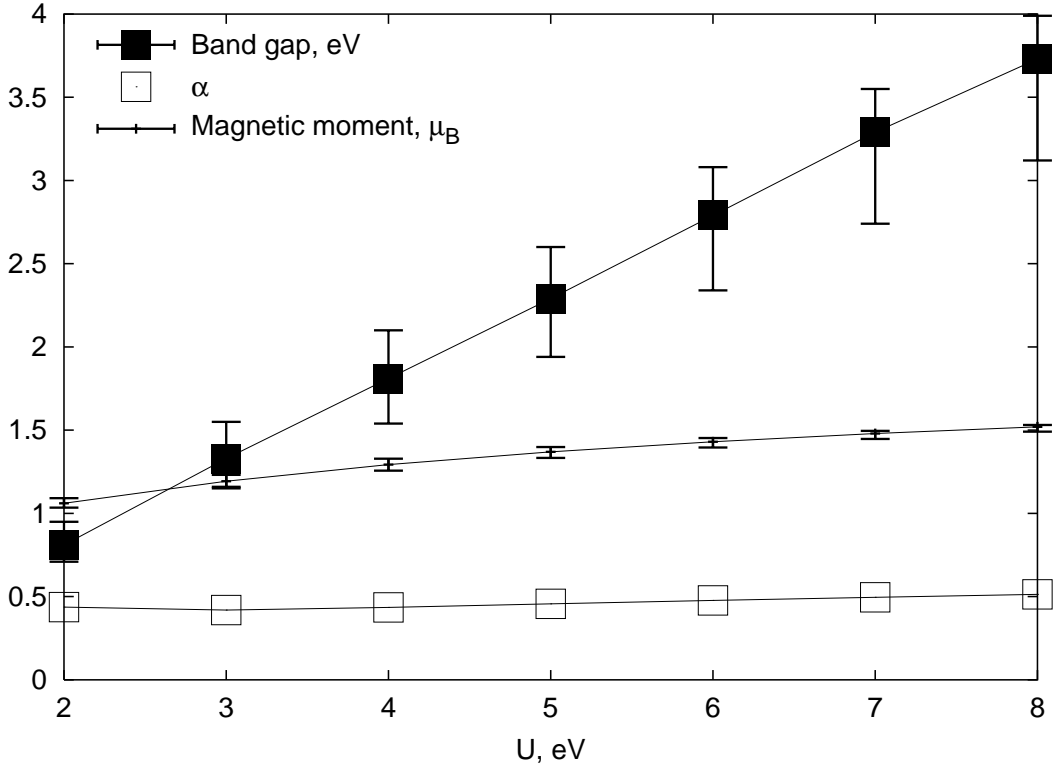


FIG. 1: Mott-Hubbard band gaps, and magnetic moments of antiferromagnetic NiO for three flavors of LDA+U. The upper and lower values of the “error bars” correspond to the FLL and AMF functionals, respectively.

Our next example is a weakly correlated metal FeAl. This paramagnetic material has attracted attention due to a recent suggestion by Mohn et al. [2] that the short-range Coulomb correlations within the LDA+U may be responsible for suppression of ferromagnetism found in all LDA calculations. More specifically, they found in their AMF LDA+U calculations a reduction of the density of states (DOS) at the Fermi level, D_F , which was sufficient to make the Stoner criterion smaller than 1 and stabilize the paramagnetic state. To analyze

this result, it is important to revisit the Stoner theory for the LDA+U case.

In DFT, the Stoner parameter I is defined as $I = -2\partial^2 E_{xc}/\partial M^2$, the second derivative of the exchange-correlation energy with respect to the total magnetic moment. The paramagnetic ground state is unstable when $D_F I \geq 1$. This can be derived from the force theorem, which states that the total energy for small magnetizations can be computed by assuming a rigid shift of the bands by $b = \pm M/2D_F$, so that the gain in the interaction energy, $-IM^2/4$, competes with the loss in the one-electron energy, $M^2/4D_F$. In the LDA+U the criterion holds, but the product $D_F I$ changes, not only because D_F changes, but also because the newly added interaction energy depends on M . Indeed, the force theorem calls for a change $\delta\rho_{mm'}^\sigma = b\sigma D_{mm'}$, where $D_{mm'} = -\pi^{-1}\text{Im } G_{mm'}(E_F)$. When applied to the functionals Eq. (2) - Eq. (4), it generates a change in the interaction energy, which results in an additional contribution to the Stoner parameter,

$$\Delta I(\alpha) = (U - J) \left(\text{Tr}(D \cdot D) - \frac{(1 - \alpha)(\text{Tr} D)^2}{(2l + 1)D_F^2} \right) \quad (6)$$

In the limit of the uniform occupancy, Eq. (6) for the FLL case ($\alpha = 1$) reduces to $(U - J)/(2l + 1)$. Given that the LDA Stoner parameter, I , is of the same order as J , we obtain for the total Stoner parameter $I_{FLL} \approx (U + 2lJ)/(2l + 1)$, which is the well known expression for the Stoner factor in the atomic Hubbard model. On the contrary, ΔI_{AMF} ($\alpha = 0$) in this limit is zero. In real metals $D_{mm'}$ is complicated due to crystal field effects. Let us consider, for illustration, d-electrons in a cubic environment, and introduce the difference $\Delta D = D_{eg} - D_{t2g}$, where D_{eg} and D_{t2g} are e_g and t_{2g} DOS per orbital at E_F , as a measure of the crystal field. This gives rise to a contribution to $\Delta I_{AMF} = \frac{5}{24}(U - J)(\Delta D/D_F)^2$. However, when LDA+U reduces D_F , and ΔI_{AMF} is not large enough to overcome the decrease in D_F , LDA+U may stabilize the paramagnetic state(cf. Ref. [12]), as, for instance, observed in a very narrow range of large U 's for FeAl by Mohn *et al.* [2] (of course, only in the AMF functional; the FLL functional produces a large $\Delta I \approx (U - J)/5$, always increasing the tendency to magnetism).

With this in mind, we performed LMTO-ASA calculations for all three LDA+U functionals, using fixed $J = 0.95$ eV. The results for U -dependence of the magnetic moment and α are shown in Fig. 2 and compared with those by Mohn *et al.* [2]. In our AMF calculations we also found a paramagnetic solution for $U = 4.85$ eV, which however coexists with a ferromagnetic high spin solution (Fig. 2). Note that for well localized orbitals there is no

difference whether the $(U - J)$ term is applied inside the atomic sphere or only inside the MT sphere, as in Ref. [2]; however, in less localized cases, where a noticeable part of the d -orbitals spills out of the MT sphere, the effect of the same U is smaller when applied only inside the MT sphere. One can see in Fig. 2 that, indeed, our calculations with large U yield large α 's and agree very well with Ref. [2], while for small U (small α) the effect of U in our ASA calculations is stronger than in Ref. [2].

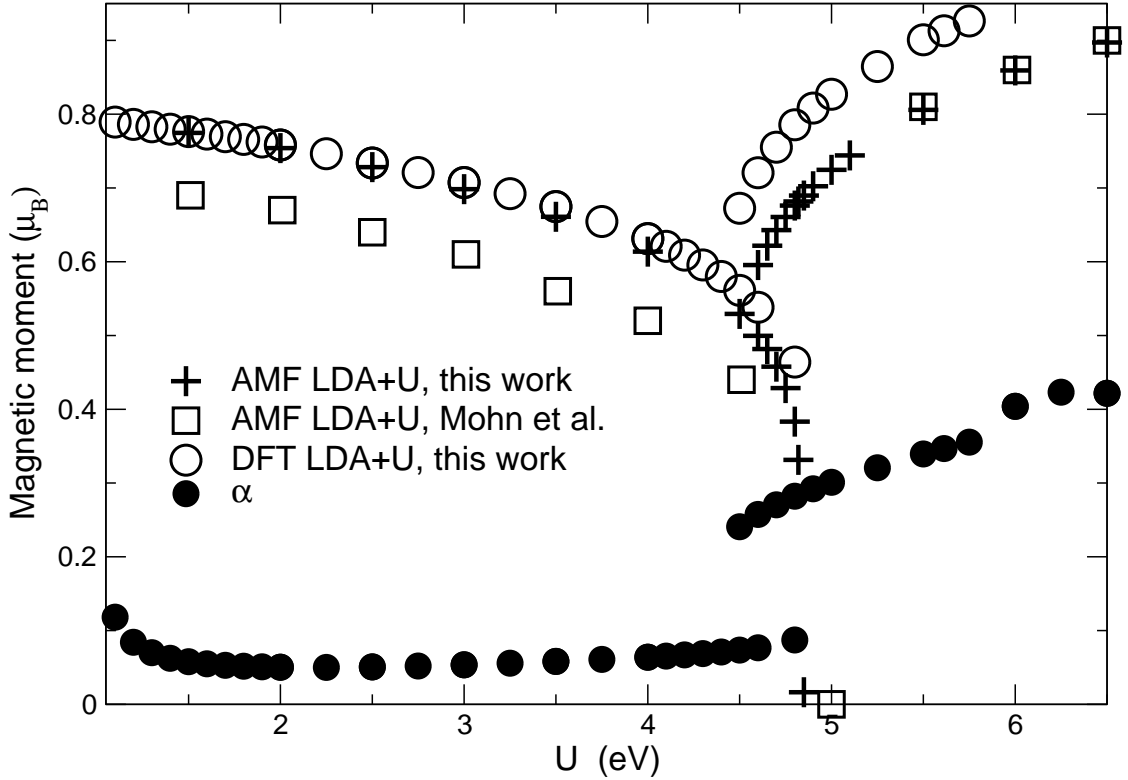


FIG. 2: Magnetic moments of FeAl for AMF and DFT flavors of LDA+U compared with the results of Mohn et al. (Ref. [2])

All LDA+U functionals shift unoccupied bands up and occupied bands down. Therefore LDA+U broadens the bands crossing the Fermi level. Because of this broadening, in FeAl for small U the parameter α is initially decreasing (Fig. 2) with a minimum $\alpha = 0.05$ at $U = 2$ eV. The magnetic moment also decreases in this region. At larger U , α starts growing again. At this point it is instructive to apply the logic of the constrained LDA approach in which for every fixed α the total LDA energy is minimized under the constraint $\sum_{\sigma} \text{Tr}(\delta\rho^{\sigma} \cdot \delta\rho^{\sigma}) / [(2l + 1) \sum_{\sigma} n_{\sigma}(1 - n_{\sigma})] = \alpha$, $(U - J)/2$ being the Lagrange multiplier. For $\alpha \leq 0.087$ (Fig. 2) of the two possible solutions with $U < 2$ eV and $U > 2$ eV we should

choose the one with lower energy (smaller U). As a result, we find two admissible domains for U : an AMF-like with $U < 2$ eV and a FLL-like with $U \gtrsim 5$ eV. The latter is clearly unphysical. Both solutions are ferromagnetic. The solutions with intermediate values of U and reduced magnetic moments are inadmissible in the framework of the constraint DFT formulation.

On the contrary, our explanation of the paramagnetism in FeAl is that the ferromagnetism instability is suppressed by the critical spin fluctuations. There are many other systems for which the fluctuations in the vicinity of a quantum critical point reduce the tendency to magnetism. Further examples include $\text{Sr}_3\text{Ru}_2\text{O}_7$ ($M_{LDA} \approx 0.8 \mu_B$, $M_{\text{exp}} = 0$), ZrZn_2 ($M_{LDA} \approx 0.7 \mu_B$, $M_{\text{exp}} = 0.2 \mu_B$), and other. The physics that is missing from both LDA and LDA+U equations in such systems can be described as exchange of virtual electronic excitations, roughly speaking, plasmons or (para)magnons. This leads to “dressing” of the one-particle excitations in the same way as the electron-phonon coupling “dresses” electrons near the Fermi surface, although in a correlated metal such mass renormalization effects occur on a large energy scale (of the order of U or J). LDA calculations cannot reproduce such a dressing, which has been observed in many different ways experimentally. For instance, LDA calculations do not explain large mass renormalizations in Sr_2RuO_4 [13], and large specific heat renormalization in many correlated metals, produce too large plasma frequencies, *e.g.*, in $\text{YBa}_2\text{Cu}_3\text{O}_7$, yield an optical absorption spectrum in CrO_2 shifted by about 20% to higher frequency, as compared with experiment [14], and overestimate the exchange splitting in Ni by a factor of 2 [15]. In all these cases the total width of the d -bands is *decreased*, as opposed to *broadening* inherent to LDA+U. Here the essential physics is missing from the LDA+U as well as in LDA, while the spatial variation of the mean-field Coulomb interaction is treated better by the LDA. The missing physics is associated, to a large degree, with dynamic fluctuations.

The dynamic version of the LDA+U method, the Dynamic Mean Field Theory (DMFT) [16], which can account for some spin fluctuations [17], resolves many of these problems. For instance, the mass renormalization in Sr_2RuO_4 is 3-4 [13], far greater than possible renormalization due to the phonons. We applied all three flavor of LDA+U to Sr_2RuO_4 and found no mass renormalization compared to LDA. On the other hand, Eliashberg-type calculations [18] of the renormalization due to spin fluctuations, using a spectrum deduced from the LDA band structure, give mass renormalizations of the right order. Similarly,

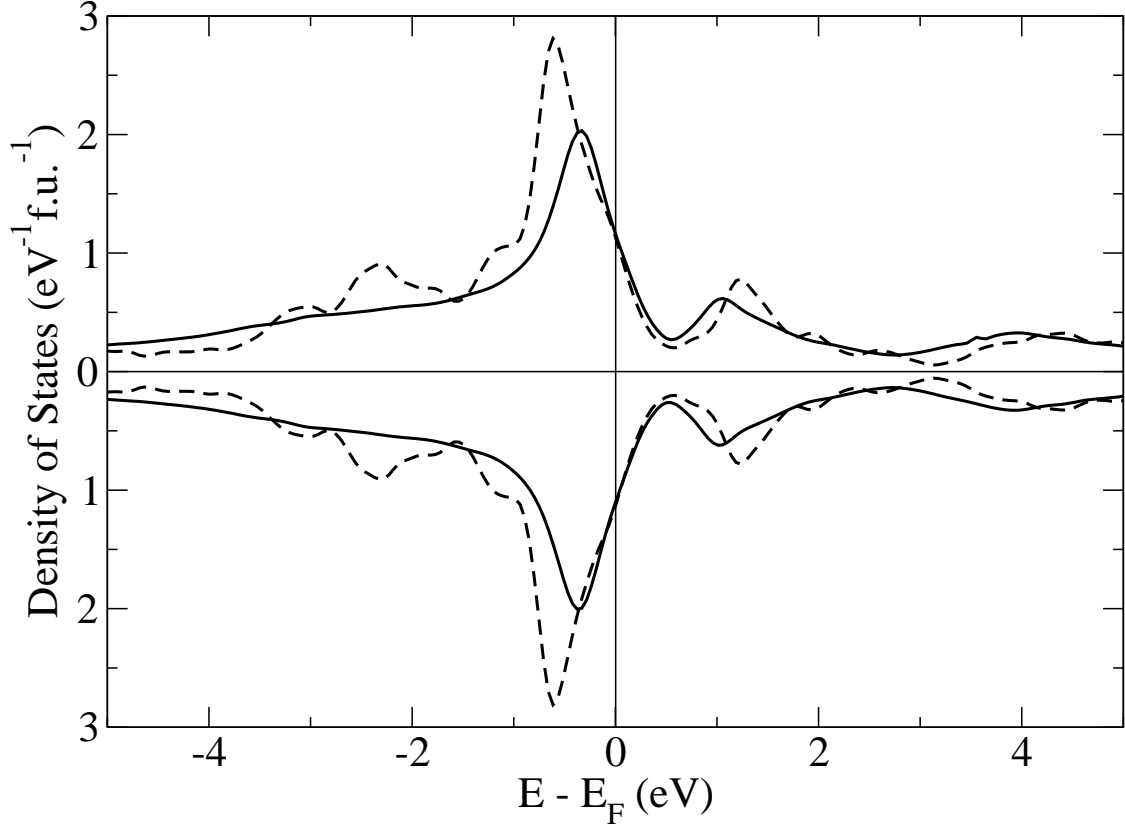


FIG. 3: FeAl density of states, $D(E)$, in DMFT (solid line) compared with the nonmagnetic LDA. The DMFT solution is stable, the LDA is not (a ferromagnetic solution is stable), despite the same $D(E_F)$.

DMFT explicitly narrows the bands in Sr_2RuO_4 and enhances the electronic mass [19]. With this in mind, we applied the DMFT with a realistic $U = 2$ eV to FeAl and found the paramagnetic state to be perfectly stable, with the bands *narrower* than in LDA, and the density of states practically the same (Fig. 3). In other words, the spin fluctuations effectively reduce the Stoner factor I .

To conclude, we observe that no LDA+U functional correctly describes the essential physics of the weakly correlated metals: (i) reducing the band dispersion by dressing of the one-particle excitation, and (ii) spin fluctuations near the quantum critical point. One functional, labeled FLL here, correctly describes the important physics in the limit of well localized electrons, and can be recommended in this case. The other functional, labeled AMF, is exact in a hypothetical material with the uniform orbital occupancies. Although neither functional accounts for the fluctuation effects, LDA+U may be useful, if applied

with a grain of salt, in moderately correlated metals. For this case, we propose a recipe that accounts for an incomplete localization and reduces to AMF or FLL in the appropriate limits. Finally, it is worth noting that in many correlated materials the spin-orbit interaction plays a key role. Since our α does not depend on spin, this prescription can be also formulated in terms of the full $(4l + 2) \times (4l + 2)$ occupation matrix ρ and $n = \text{Tr}(\rho)/(4l + 2)$. Eq. (5) should be replaced with $\text{Tr}(\delta\rho \cdot \delta\rho) = (4l + 2)\alpha n(1 - n)$. This formulation has another advantage in the case of a half-filled band, like in Gd, because in this limit it reduces to more physically meaningful in this case FLL, rather than to AMF as the nonrelativistic Eq. (4).

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